XIV.—*On Erbium and Yttrium.*

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(Preliminary Remarks.)

In 1794, after examining the mineral known as gadolinite, Gadolin announced the discovery of a new earth therein. This new earth has been shown by subsequent researches to be a mixture of at least six different substances. Ekeberg, in 1802, separated glucina, and Berzelius discovered ceria in 1815, and yttria some years later. Berlin worked with the crude yttria in 1835, which he prepared according to Berzelius' method. But although he prepared many salts, he mentions no suspicion of there being more than one earth included under this group. (*K. Vet. Akad. Hand.*, 1835, 209; and *Pogg. Ann.*, **43**, 105.)

A few years later Mosander stated that the cerium metals were three—cerium, lanthanum, and didymium; and in 1843, that the yttrium metals were also three—yttrium, erbium, and terbium. The pale rose-colour which the salts of the mixed oxides present after the separation of the cerium metals had been previously noticed,* and had been generally ascribed to manganese, the tint of whose salts it almost exactly resembles. Berzelius (*Lehrbuch*—German Edition, 1832, p. 214) mentions the occurrence of manganese, and Berlin found it in one analysis, but only in traces; otherwise the former general acceptance of the presence of this substance may be ascribed to the colour of the erbium salts.

In Mosander's original paper, which was read at a meeting of Scandinavian philosophers (*Ann. Chem. Pharm.*, **48**, 210), his description of the methods he employed for the preparation of the three earths in a state of purity is exceedingly imperfect. He says a partial separation may be effected by fractional precipitation with ammonium or potassium oxalate; yttria being the strongest base remains longest in solution, and by repeating the method many times, this earth may be obtained in a state of purity. He gives us no means of judging how this was known to be pure, or of any special method for separating the other two; he mentions nothing distinctly. Nevertheless, he gives the following as the properties of the three oxides:—

Yttria is colourless and the strongest base, its salts are colourless; terbia is colourless, and the next in basicity, its salts are reddish;

* Heinrich Rose [*Pogg. Ann.*, **59**, 101] mentioned this pink colour, and thought it might be due to some new substance, but gave up his work on hearing that Mosander and Berzelius were extending their researches.

erbia is deep-yellow in colour, becoming colourless when glowed in hydrogen without appreciable loss in weight,* its salts are colourless. Terbia is distinguished by a sulphate efflorescing at 50°.

Some years afterwards Berlin (*Fordhandlinger ved de Skan. Naturfor. attende Möde i Kjöbenhavn*, 1860, p. 418) subjected these earths to a new examination. Following the method of separation proposed by Mosander, he was able to obtain only two earths, yttria and erbia; his terbia was always capable of being resolved into the other two, when the separation was continued long enough. He was also unable to obtain the sulphate efflorescing at 50°, which Mosander mentioned as being characteristic of terbia.

In 1864, Popp (*Ann. Chem. Pharm.*, **131**, 179), under the direction of Woehler, published some further researches, but as he considered that the crude yttria contained only one earth, we need not delay discussing his results.

The year following, Delafontaine (*Ann. Chem. Pharm.*, **134**, 99), after carefully repeating Mosander's method of separating the crude yttria, confirmed the results of this chemist. But as he adopted Berzelius' method of separating the cerium metals, and did not allow the solution of the sulphates to remain in contact with the potassium sulphate longer than twenty-four hours, it is clear that his crude yttria must have contained considerable quantities of these three earths; and as he distinctly says that his potassium-erbium sulphate is insoluble in a saturated solution of potassium sulphate, we may fairly conclude that his erbia consisted mostly of the oxides of the cerium metals. This supposition is strengthened by the fact that the atomic weight which he gives for this erbium (95·36) coincides almost exactly with the mean of those of the cerium metals (94·00). Several properties of this substance agree also remarkably with those of the cerium metals, among which may be mentioned the fact that its salts give an absorption-spectrum resembling that of the didymium salts, except that the lines are not so intense. In a later paper (*N. Arch. Ph. Nat.*, **25**, 112, 1866) he corrects his statement, but mentions that his erbium-salts have all a pink colour. From analyses of the sulphates he gives the following atomic weights:—

$$Y = 111{\cdot}6\,;\ Er = 143{\cdot}04\,;\ Tr = 137{\cdot}04\ [\text{oxides} = M_2O_3],$$

though he does not himself consider these results very accurate. Yttria is white, erbia yellow, and terbia pink.

In the following year Bunsen worked at the subject in conjunction with a Swedish chemist, Bahr. They found that the best method of separating the crude yttria was by means of the basic nitrates. This method consists in dissolving the mixed basic nitrates in the smallest possible quantity of hot water, when the crystallisation, which

* A fact first noticed by Scheerer.

separates out on cooling, is always richer in erbium than the material employed. In this way, by working a number of series of crystallisations, they obtained two earths in a state of purity, to which they give the names erbia and yttria. All search for the third earth (Delafontaine's erbia) was fruitless. They published for the first time a drawing of the absorption-spectrum of the erbium salts, and by a comparison with that of the didymium salts, showed that no two lines coincided with one another. They made the interesting discovery, which Bahr had before casually observed, that when erbia is heated to whiteness, it emits a green light and gives a bright spectrum exactly the inverse of the absorption-spectrum of its salts. They found, too, the same to be the case with didymium oxide. The following atomic weights are given:—

$$Y = 92{\cdot}55;\ Er = 168{\cdot}9;\ [\text{oxides} = M_2O_3].$$

Cleve and Hoeglund (*Bull. Soc. Chim.*, 1872, **18**, 193) have published some interesting work on these substances. They attempted the extraction of the metals by electrolysis, but obtained nothing but black powders. We are indebted to them for descriptions of a large number of salts prepared from erbia and yttria carefully separated by Bunsen's method. They searched in vain for the third earth. As atomic weights they give the following numbers:—

$$Y = 89{\cdot}55;\ Er = 170{\cdot}55.$$

The difficulty of obtaining the earths in such a state of purity is instanced by the fact that, although they employed five kilograms of gadolinite, they obtained only a few grams of the pure oxides. From the constitution of the salts which they prepared, it would appear that the metals are triatomic, *i.e.*, the oxides are sesquioxides.

In the beginning of this year Marignac published some investigations on these earths (*Arch. Scien. Ph. und Nat.*, **61**, March, 1878). He extracted them as usual from gadolinite, and employed Bunsen's mode of separation, *i.e.*, by means of the basic nitrates. Following this out carefully, he obtained, as the two end-products of a long series of crystallisations, a rose-coloured and a white oxide, Bunsen's erbia and yttria. But besides these two he noticed that the middle products were much deeper in colour than the original mixed oxides, even when a trace of the cerium metals had been removed. These deep-coloured middle products he divided into two classes, (1) those containing erbium in considerable quantity; and (2) those containing only traces of this substance. He found no method of separating the erbium from the first class, but was able to separate the yttrium from the second, by successive fractional precipitations with oxalic acid, the yttrium remaining longer in solution. By this means an earth was obtained

becoming deeper and deeper in colour. Solutions of this earth are colourless, and give no absorption-spectrum. This should be the missing erbia of Mosander, Bunsen's terbia. Careful determinations of its atomic weight gave

$$Tr = 148{\cdot}5\,;\ [\text{oxide} = Tr_2O_3].$$

In the same Journal, of the same date, M. Delafontaine has published some further work on the earths contained in samarskite. After removing the cerium metals, he first effected a partial separation with oxalic acid, then dissolved the deep-coloured oxides so obtained in formic acid, which on heating gave a precipitate whose oxide was still deeper in colour. By continuing this separation he at last obtained an oxide, the metal of which gave the atomic weight 147, a number agreeing very well with that found by Marignac for terbium.

We have instituted some further experiments with these earths, with the special object of isolating the metals and determining their specific heats; hoping, too, to find a better method of separation than is at present known.

We made use of gadolinite for the extraction of the earths. For this rare material we are indebted to Professor Bunsen, and to Professor Waage, of Christiania, to whom we wish to tender our sincere thanks.

The crude earths were extracted in the usual way, and the separation of the cerium metals carefully performed by dissolving the anhydrous sulphates in fifteen parts of ice-cold water, and then suspending in this solution masses of potassium sulphate, so arranged that portions of the salt projected out of the liquid. This was allowed to stand for about a fortnight, the liquid being frequently agitated. At the end of this time the liquid, which did not show the spectrum of the didymium salts in the faintest degree, was filtered, and ammonia added in excess. The precipitate so obtained was then dissolved in hydrochloric acid and reprecipitated with oxalic acid. This precipitate on glowing gave the pure earths. There were still very slight traces of the cerium metals present, which were afterwards specially removed. The oxides were specially tested for manganese, but not a trace was found.

The crude yttria so prepared was a light, pale lemon-coloured powder, easily soluble in all acids.

With regard to the separation of these mixed earths, we regret that we have as yet been unable to find a better method than the approximate one with the basic nitrates, as employed by Bunsen. The process is an exceedingly tedious one, and the pure oxides are obtained only in very small quantities, even when considerable masses of material are employed.

As the special object of these investigations was to determine the

true atomic weights of these elements, a long series of experiments was made to procure the metals in coherent masses, and determine their specific heats. Here, again, only negative results were obtained. All attempts to decompose the fused chlorides by electrolysis have yielded the metals only as black powders, or as small metallic scales. The same method was followed as that employed by Bunsen for preparing calcium, strontium, &c. The chlorides were prepared, just like anhydrous magnesium chloride, by evaporating their solution with a large excess of sal-ammoniac, and then driving off this latter by heat. The black mass at the end of the electrolysis, on being powdered under, and washed with naphtha, always left a heavy black powder, with many bright metallic scales, nearly resembling aluminium. This was slowly oxidised by water at the ordinary temperature; more rapidly on warming, with a brisk evolution of hydrogen. The action was, of course, accelerated by dilute acids. The metal burnt in the flame of a gas-lamp with a brilliant white light, like magnesium. We also obtained in nearly every operation some small bright-red, transparent crystals, decomposed slowly by water and acids, but otherwise tolerably stable. This may have been an oxychloride corresponding with that of didymium; we did not obtain sufficient quantities of it to make a thorough examination.

As the specific heat of the metals could not be obtained, and as no volatile compound of these elements is known, the next best method of finding the atomic weights is by isomorphism.

As far as we know, the only salts which have been carefully investigated are the sulphates.

Rammelsberg (*Pogg. Ann.*, **115**, 579) has shown that the sulphates of didymium and of the mixed yttrium metals have a chemical composition similar to that of cadmium sulphate, and that the angles of the three salts agree tolerably well. From this he drew the natural conclusion that the oxides of yttrium and didymium were monoxides, which, as far as the latter is concerned, the later researches of Hildebrand and Norton (*Pogg. Ann.*, **158**, 71) have not confirmed. We cannot tell whether this, too, may be the case with the yttrium metals, which seems probable, or whether the atomic weight derived from the isomorphism with the cadmium salt is to be accepted. A glance at the numerous compounds prepared by MM. Cleve and Hoeglund shows that they are formulated in the simplest manner on the supposition that the oxides are sesquioxides, and it need scarcely be remarked that the analogy of the yttrium salts to those of didymium is far greater than to those of cadmium. We have further experiments in progress to decide this question of isomorphism.

By conducting a long series of crystallisations we were able to obtain some erbia, giving a combining weight of 195·84 (mean of four

determinations); this on being subjected to crystallisation in the usual manner gave a product the combining weight of whose oxide was 195·61 (mean of 195·54 and 195·69).* These numbers agree so well together as to make it more than probable that this was pure erbia. Comparing the atomic weight of erbium so obtained with previous determinations of other chemists, we have:—

Delafontaine	= 137·04	
Bunsen and Bahr.....	= 168·90	
Cleve and Hoeglund	= 170·55	mean = 171·08.
Humpidge and Burney	= 171·61	

As Delafontaine employed Mosander's method of separation, which yields only very approximate results, we may disregard his number; and as Bunsen worked with only comparatively small quantities, his erbia may not have been perfectly pure. It is therefore extremely probable that the atomic weight of erbium lies between our determinations and those of Cleve.

We have not as yet obtained any yttria sufficiently pure to be able to make an accurate determination of its combining weight.

At the end of this paper are two analyses of the gadolinite we have employed. One specimen was from Ytterby, and the other from Hitterö. The question of the presence of manganese has been already touched upon, and with regard to glucinum, we may remark that the older methods of extracting the crude yttria did not completely separate this substance. Heinrich Rose (*Pogg. Ann.*, **59**, 101) was the first to remark that this was the case, and to show that the chlorides are not volatile. Woehler's yttrium (*Pogg. Ann.*, **13**, 580) must therefore have been glucinum, as it was prepared from a volatile chloride. He says, too, that the metal so prepared does not decompose water at the ordinary temperature, whereas that prepared by electrolysis of the pure chlorides always does so. The presence of phosphoric acid in gadolinite is, as far as we know, mentioned for the first time. It was probably all or nearly all present as phosphates of the yttrium and cerium metals, as it nearly all remained behind on decomposing the mineral with *aqua regia*. These earths remaining behind with the silica consisted of nearly pure yttria with traces of the cerium metals.

Thinking perhaps that we might be able to find some xenotime enclosed in the gadolinite, we prepared several microscopic sections of the mineral, but nothing was to be seen except a dark-green homogeneous field, without action on polarised light:—

* (i.) Oxides = 1·2147 gram. Sulphates = 1·9596 gram.
(ii.) Oxides = 1·1781 „ Sulphates = 1·9011 „

	(1.) Gadolinite from Ytterby.	(2.) From Hitteröe.
SiO_2	25·161	24·242
P_2O_5	1·281	—
Yt_2O_3	35·160	30·588
Er_2O_3	4·109	10·908
Ce_2O_3, La_2O_3, Di_2O_3	6·521	9·926
Be_2O_3	9·388	6·564
Fe_2O_3	2·150	—
FeO	12·401	16·040
CaO	1·106	0·787
MgO	traces	0·236
K_2O	—	traces
H_2O	2·321	0·620
	99·598	99·911

The specimen from Ytterby was much more easily decomposed by acids than that from Hitteröe, even cold hydrochloric acid sufficing for its decomposition. The high percentage of glucinum in the former, combined with the fact that this specimen was entirely without action upon polarised light, does not agree with Des Cloizeaux's hypothesis that the amorphous gadolinites are free, or nearly so, from glucinum.

The above experiments were mostly made in Professor Bunsen's laboratory, and we wish to express our hearty thanks for his continual help and guidance.

Addendum.—The above paper was written before the publication of the latest researches of MM. Marignac and Delafontaine.* Whether the new earths that have been announced by these chemists really exist in the crude yttria must still be a matter of doubt, particularly the "philippia" and "decipia" of M. Delafontaine, about which so few details are given. To decide whether the "ytterbia" and terbia of M. Marignac really exist, further experiments are necessary, with which we are at present engaged, and which will form the subject of another communication.

* See Abstracts, pp. 113—118.